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Electrochemical Reduction of Energetically Contaminated Wastewater

Development and Testing of Pilot Scale Reactor

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Stephen W. Maloney, and George Sorial

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Foreword

This study was conducted for Headquarters, U.S. Army Corps of Engineers (HQUSACE) under Project 4A162720D048, "Industrial Operations Pollution Technology"; Work Unit U00, "Electrochemical Reduction of Nitro-Aromatic Compounds." The technical monitor was Chris Vercautren, OSC, Rock Island, IL.

The Environmental Processes Branch (CN-E) of the Installations Division, U.S. Army Construction Engineering Research Laboratories (CERL) performed the work. The study was performed in part by the University of Cincinnati, Cincinnati, Ohio, under contract to the Environmental Processes Branch. The USACERL principal investigator was Dr. Stephen W. Maloney. The associated Technical Director was Gary W. Schanche. Dr. Ilker R. Adiguzel is Chief, CECER-CN-E; and Dr. John T. Bandy is Division Chief, CECER-CN. William D. Goran is Acting Director of CERL.

CERL is an element of the U.S. Army Engineer Research and Development Center (ERDC), U.S. Army Corps of Engineers. The Director of ERDC is Dr. James R. Houston and the Commander is COL James S. Weller.

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1 Introduction

Background

The major constituents of munitions production wastewaters are 2,4,6 – trinitrotoluene (TNT), 2,4 – dinitrotoluene (DNT), and hexahydro – 1,3,5 – trinitro – triazine (RDX). DNT is found in wastewaters from propellant production, whereas TNT and RDX enter waste streams during munitions loading and demilitarization. The waters contaminated by TNT and RDX are commonly referred to as "pinkwater," due to their characteristic color. Over 1200 Department of Defense (DOD) sites have explosive contamination (Draft Program User Review 1992), most of which are contaminated by TNT. Of these sites, many also have contaminated the groundwater. Most of these sites have been found to contain a significant amount of explosives in soil and water samples (Jenkins et al. 1993), the major contaminant being pinkwater generated by "load, assemble, and pack" and demilitarization operations that were conducted in the 1970s. Both TNT and DNT are listed as priority pollutants by the U.S. Environmental Protection Agency (USEPA) because of their toxicological hazards.

DNT is used commercially as an intermediate in the manufacture of toluene diisocyanate, which is then used in the production of polyurethane foams. DNT is also used as an ingredient in military and commercial explosives. For military purposes, DNT is primarily used as a plasticizer and burn rate modifier in single base propellants. DNT is prepared by the nitration of toluene and nitrotoluene in the presence of nitric and sulfuric acids.

TNT is the most widely used explosive in the world because of its low melting point (80.1 °C), stability, low sensitivity to impact, and relatively safe methods of manufacture compared with other explosives. TNT is a high explosive and is used in bombs and grenades in binary mixture with a primary explosive to trigger the explosion. It is also used for deep water and underwater blasting. TNT is prepared by the nitration of toluene with a mixture of nitric acid and sulfuric acid (Fisher et al. 1983). It enters waste streams during manufacturing, loading, and assembling and packing operations.

RDX is used in artillery shells as a high explosive and also in combination with TNT. It acts as a good explosive because of its higher density, lower flame temperatures and release of higher energy.

Objectives

The general goal of this study was to evaluate the performance of a pilot reactor for electrochemical reduction of simulated propellant wastewater (DNT 100 mg/L and ethanol 300 mg/L) and pinkwater (TNT 70 mg/L and RDX 10 mg/L). The specific objectives of this study were to provide information regarding: (1) the kinetics of electrochemical reduction of simulated propellant wastewater (DNT 100 mg/L and ethanol 300 mg/L) and pinkwater (TNT 70 mg/L and RDX 10 mg/L) at various currents and stir-rates; (2) the impact of the presence and absence of dissolved oxygen on the electrochemical reduction rates; and (3) the performance of a continuous flow pilot scale reactor at various currents and flow rates for the reduction of these compounds of interest.

Approach

Kinetic determination of reduction of nitroaromatics was studied in a bench-scale electrochemical batch reactor, which was fabricated in previously reported studies. The rate of electrochemical reduction was measured under various experimental conditions including current density, stir rates, and the presence and absence of dissolved oxygen. Electrochemical reduction of these nitroaromatic compounds in a continuous system was studied by using a pilot scale plug flow reactor, which was fabricated during the current study. The by-products of electrochemical reduction of DNT were identified by gas chromatography (GC), and of TNT and RDX by High Pressure Liquid Chromatography (HPLC). For the batch experiments, a mass balance for the products was obtained under a variety of experimental conditions both in the aqueous and the solid phases. The reduction behavior was then assessed in light of the experimental results, and conclusions were drawn from the data to address the objectives of the research.

Scope

The techniques described in this report apply to Army industrial activities. The agencies responsible for development and treatment of Army-specific explosives and other aqueous waste streams will benefit from the information presented

here. The goals of developing and understanding new treatment technology potentially applicable to nitrated explosives are addressed.

Mode of Technology Transfer

It is anticipated that the results of this basic research will lead to the testing of a portable bench scale reactor on site with actual Army wastewaters.

2 Literature Review

An explosives contamination problem in soil and groundwater was identified at many U.S. Department of Energy and Department of Defense sites. TNT is the most commonly found explosive in most of these sites, though DNT is also frequently found at munitions-contaminated sites. Both DNT and TNT have been listed as priority pollutants by the USEPA because of their toxicities. The LD_{50} value in rats for DNT is 268 mg/kg (Sax et al. 1989).

Biological Pathways

Extensive studies have been done on the biological degradation of the various nitroaromatics. The biological degradation of chemicals can be divided into two main categories — aerobic and anaerobic degradations. Both kinds of reactions have been shown to successfully degrade some nitroaromatics. Reduction is the most common mechanism and takes place when the nitroaromatic compound is reduced to arylamines.

Pseudomonas species is shown to degrade both DNT and TNT aerobically with supplemental glucose as the carbon source (Parrish et al. 1977). Haidour et al. showed that *Pseudomonas* species clone A performs two different types of reduction processes with TNT. One process leads to the removal of a nitro group and allows its utilization as an N-source, while the other leads to unproductive compounds. They also identified the various intermediates formed during the biodegradation of TNT and DNT using *Pseudomonas* species. Berchtold et al. (1995) designed a fluidized-bed anaerobic granular activated carbon reactor, which effectively transformed DNT to diaminotoluene (DAT). They also showed that conversion of DNT is unaffected by influent ethanol concentration, though 200 mg/L of ethanol was determined to be the minimum concentration of ethanol needed to affect the reduction of DNT to DAT. The DAT formed was then successfully degraded below detection levels using a second stage, activated sludge reactor.

Studies done by Boopathy et al. (1993) observed the performance of anaerobic soil bacterial consortium to remove TNT in the presence of various electron acceptors. They observed that a significant amount of TNT was removed in the enrichment culture that used nitrate as electron acceptor. They also showed

that the main intermediates of TNT degradation are 2-amino-4,6-dinitrotoluene and its isomer 4-amino-2,6-dinitrotoluene.

Young et al. (1996) observed the biotransformation of RDX in liquid culture by a consortium of bacteria found in horse manure. Five types of bacteria were found to be predominant in the consortium. The most effective bacteria at transforming RDX was observed to be *Serratia marcescens*. Observations of the mole balances indicate that the first step of RDX biotransformation is the conversion to mono-, di-, and tri-nitroso substitutes of nitro groups in RDX – commonly called MNX, DNX, and TNX, respectively. Kitts et al. (1994) observed that one pathway for the biotransformation of RDX was a stepwise reduction of each of RDX's three nitro groups to form nitroso groups. They isolated three different genera of bacteria capable of degrading RDX, the most effective being identified as *Morganella morganii*.

Electrochemical Pathways

Many studies have been carried out on the electrochemical reduction of nitro-organics. Electrochemistry, with its unique ability to reduce compounds at a well-controlled electrode potential, offers many interesting possibilities in environmental engineering (Simonsson 1997). Electrochemical reduction involves the reduction of the nitrogen in the nitro group, which is already at a high oxidation state of +3. There is no known electrochemical oxidation of DNT, since it is very difficult to remove an electron (Fry 1982).

Willberg et al. (1996) explored the oxidation of TNT in an electrohydraulic discharge reactor. They also observed that the addition of ozone to the electrohydraulic discharge reactor dramatically increased the TNT degradation rate and caused greater than 99 percent degradation. This enhancement was attributed to the reaction of TNT with the hydroxyl radicals produced by the photolysis of ozone since the dark reaction of TNT with ozone is very low.

Electrochemical techniques have also been explored on the treatment of industrial waste waters (Ribordy et al. 1997). Optimal values of temperature, pH, electrode characteristics, initial concentration of effluents, and NaCl used were determined and the TOC was observed to decrease by 52 percent. Martigny et al. (1983) evaluated the existence of the intermediate nitroso during the electrochemical reduction of nitro compounds. The nitrobenzene intermediate was rarely observed, though the evidence of its formation has been observed by the formation of the azoxy and azobenzene dimers. In another study (Kopilov et al. 1990), it was found that dehalogenation can occur when electrochemical reduc-

tion is applied to a haloacetanilide in alcohol and acetonitrile. These same groups (nitro- and halo-) protect the compounds from biological attack. Hence, the contaminant can be then treated using conventional biodegradation.

Other Pathways

The most common present method of destruction of the nitroaromatics is incineration. However, issues such as safety concerns, noise, air emissions, costs, regulatory requirement, etc., have motivated research in alternative technologies. The present technology used by the military ammunition plants involves the adsorption of TNT and DNT on activated carbon (Ho et al. 1988). This technology is nondestructive and expensive. Furthermore, the carbon has to be disposed of as hazardous waste, which is quite expensive.

Photochemical reduction of TNT has been studied extensively and has been considered as both primary treatment and pretreatment to bioremediation. TNT strongly absorbs UV radiation between 200 and 280 nm. When exposed to sunlight or near UV radiation, TNT rapidly converts into a variety of photolysis products. TiO_2 photocatalysis using near-UV radiation can effectively achieve complete mineralization of TNT (Schmelling et al. 1995). Photocatalytic transformation of TNT appears to involve both oxidative and reductive steps. They also concluded that, if the photocatalytic reaction is conducted using higher energy UV light, the reaction proceeds at a greater rate, but not to a greater extent.

Cheng et al. (1996) observed that DNT was abiotically reduced to 4-amino-2-nitrotoluene and 2-amino-4-nitrotoluene in the presence of a high concentration of sulfide. Sulfide served as an electron donor for the reduction of DNT. It was also observed that no reduction of DNT occurs in the presence of low sulfide concentrations and the rate of reduction increases as the concentration of sulfide is increased. They also studied the rate and extent of DNT reduction in the presence of other chemicals.

Other technologies investigated in application to TNT remediation are: clay/resin adsorption, ionizing radiation, and supercritical oxidation. The other major technique, widely reported in literature, is the catalytic hydrogenation of DNT over a Pd/C catalyst. Palladium-catalyzed hydrogenation has been found to completely reduce DNT to DAT (Janssen et al. 1990). The intermediates were observed to be hydroxylamino-2-nitrotoluene, 4-amino-2-nitrotoluene, and 2-amino-4-nitrotoluene.

3 Materials and Methods

Batch Experiments

Batch experiments were carried out in a 2.5-L glass reactor. Figure 1 shows the experimental setup (Meenakshisundaram et al. 1999 and Pehkonen et al. 1999). A Nafion membrane #117 from Solution Technology/C.G. Processing (Rockland, DE) was used to separate the anode and the cathode, and to allow the transfer of ions only and to prevent the transfer of any of the organic compounds being degraded or being formed

A Honeywell UDC 3000 Universal Digital Controller was used as a constant source of current. A Fisher Scientific (Pittsburgh, PA) Thermix Stirrer Model, along with a 2-in. Teflon®-coated stir bar, was used for all experiments. The cathode used was a glassy carbon (Sigradur G) rod, 7mm in diameter and 150mm in length, obtained from SGL Carbon Corporation (St. Marys, PA). Table 1 lists the various properties of glassy carbon cathode. A 6-in. long 18G platinum wire (Fisher Scientific) was used as the anode.
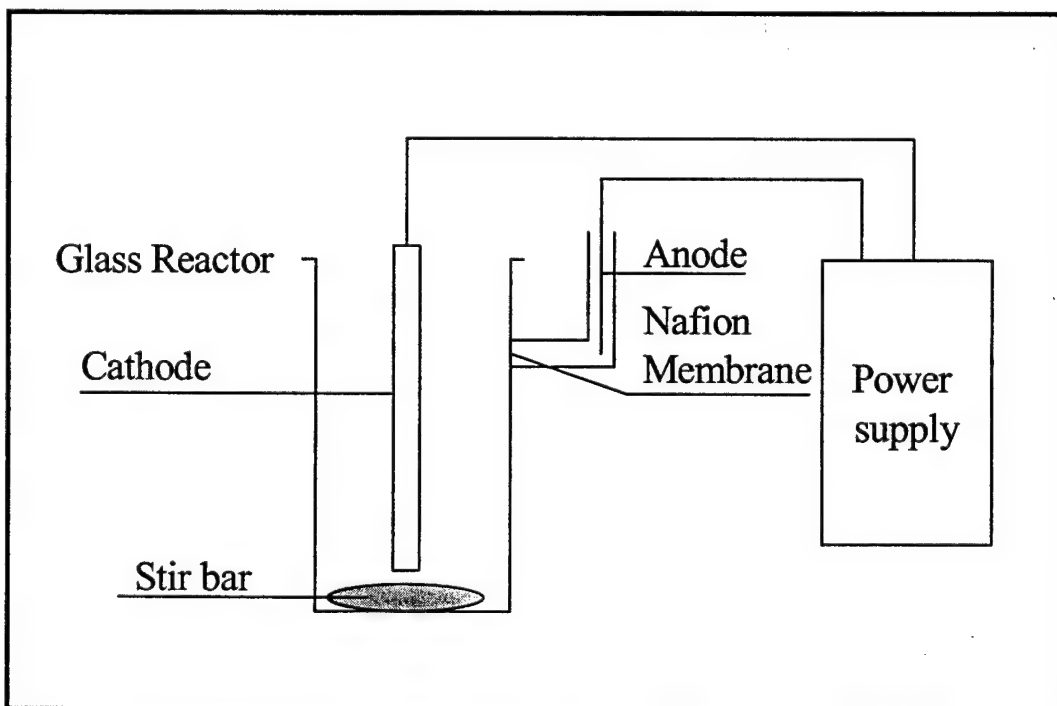

Figure 1. Experimental setup for batch experiments.

Table 1. Physical properties of glassy carbon cathode.

Property	Metric Units
Maximum grain size	—
Apparent density	1.42 g/cm^3
Total porosity	0%
Electrical resistivity	4.4 x 10^3 μ ohm-cm
Ash	0%

DNT was purchased from Aldrich Chemical Co. (Milwaukee, WI) at 97 percent pure and was used as received. 2,4,6-trinitrotoluene (TNT) and RDX were obtained from the Army and were used as received. Sodium phosphate, obtained from Fisher Scientific, was used as the buffer to maintain the desired pH. Anhydrous sodium sulfate from Fisher Scientific was added to the reactor for a constant ionic strength.

Previous reports by Meenakshisundaram et al. 1999 and Pehkonen et al. 1999 identified the various intermediates during the electrochemical reduction of DNT (with ethanol) and TNT and RDX. Hence for the quantification of the intermediates, the following chemicals were purchased:

- 2,4-diaminotoluene (DAT) was obtained from Aldrich and was used as received.
- 2-amino-4-nitrotoluene and 4-amino-2-nitrotoluene were also obtained from Aldrich and were used in the synthesis of rest of the intermediates.

For the quantification of TNT intermediates, the following chemicals were purchased from Accustandard Inc. (New Haven, CT):

- 2,4-diamino-6-nitrotoluene, obtained at a concentration of 0.1 mg/ml in acetonitrile.
- 2,6-diamino-4-nitrotoluene, obtained at a concentration of 0.1 mg/ml in acetonitrile.
- 2,2',6,6'-tetranitro-4,4'-azoxytoluene, obtained at a concentration of 0.1 mg/ml in acetonitrile: methanol (1:1).
- 4,4',6,6'-tetranitro-2,2'-azoxytoluene, obtained at a concentration of 0.1 mg/ml in acetonitrile: methanol (1:1).
- 4-amino-2,6-dinitrotoluene, obtained at a concentration of 1 mg/ml in acetonitrile: methanol (1:1).
- 2-amino-4,6-dinitrotoluene, obtained at a concentration of 1 mg/ml in acetonitrile: methanol (1:1).

Experiments were conducted in a 2.5-L glass reactor, as shown in Figure 1. The length of time for all experiments was always less than 12 hr. DNT/ethanol or

TNT /RDX were allowed to mix in 2L of water in the glass reactor for a period of 2 days before the start of the experimental run to ensure complete solubility. On the day of the experiment, required amounts of Na_2SO_4 (36 g/L) and sodium phosphate buffer (0.02 M) were added to the solution and allowed to mix for 1 hr. The experiment was then set up and started. Six to eight samples were taken at regular time intervals for each experimental run. The pH of the solution was also regularly monitored and maintained at a pH of 8. DNT and its intermediates were analyzed by GC, an HP 5890 Series II with an FID detector, 30m x 0.32mm inside diameter (i.d.) fused silica capillary column and 0.25 mm film thickness (J&W Scientific, DB-1), and a carrier gas of nitrogen (80 psi). A measured quantity (2.5 ml) of the solution is withdrawn from the reactor and then the contaminants are extracted into 0.5ml of dichloromethane, by vigorous shaking for 90 seconds, which were then used as samples for the GC. An internal standard of quinoline (25 ppm) was used for the precision analysis. For TNT, its intermediates, and RDX analysis, an HP 1050 HPLC system using a c-18 column with a quaternary pump and a UV Diode Array Detector (DAD) was used. The HPLC-18 column was eluted with 5:5 acetonitrile: water, at a flow rate of 0.7 ml/min.

Since all the intermediates of DNT are not commercially available, the intermediates were synthesized as discussed in a previous report (Pehkonen et al. 1999). The intermediates synthesized were 4,4'-dinitro-2,2'-azoxytoluene, 2,2'-dinitro-4,4'-azoxytoluene, 2-nitro-4-nitrosotoluene, and 4-nitro-2-nitrosotoluene.

Pilot Scale Continuous Flow Reactor

Figure 2 shows the experimental setup for the pilot scale flow-through reactor. The main reactor consists of two concentric cylinders. The outer cylinder, the cathode compartment of the reactor, is graphite carbon with surface impregnation of vitreous carbon (glassy carbon). It has an internal diameter of 12 cm (4.72 in.) and a height of 60 cm (23.62 in.). The carbon cylinder was fabricated by M.G.P., Inc. (Robesonia, PA). The inner cylinder is a fabricated Teflon® tube for holding the Nafion membrane in place, and has inner and outer diameters of 3.81 cm (1.5 in.) and 5.715 cm (2.25 in.) respectively. A 24-inch platinum wire, obtained from Fisher Scientific, spans through the length of the inner cylinder and acts as the anode. The two feed tanks are made of stainless steel and have a capacity of 75 L. The effluent and salt tanks are 7-gal Polyethylene tanks obtained from Fisher Scientific.
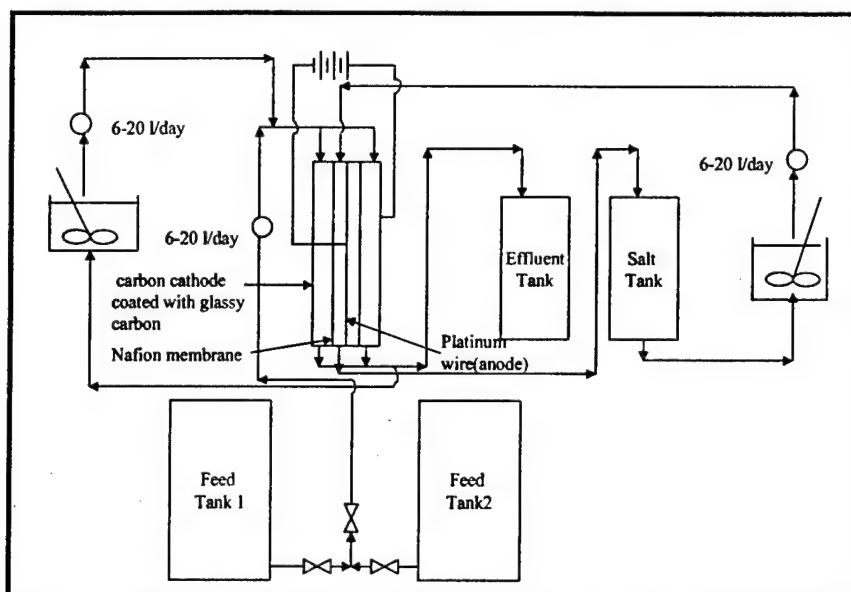
Figure 2. Schematic for electrochemical flow-through reactor.

Three pumps, with a pumping capacity of 6 to 20 L/day are used in the experimental setup. All three pumps are positive displacement pumps, obtained from the Barnant Co. (Barrington, IL), HD-MA type 01-10 with a maximum capacity of 1 L/hr. The maximum number of strokes is 100/min., which yields a maximum pressure of 142 psig, with a suction height of 1.5 m.

Two 500-mL holding stainless steel tanks are used for pH adjustment. One is used for adjusting the pH in the recycle stream and the other for the salt solution stream. These tanks have secure lids that have two ports. One port is used for the pH probe and the other port is fitted with a septum for injection of acid for pH adjustment. The mixing of feed solution was done by using high power magnetic stirrers (Thermix Stirrer Models) obtained from Fisher Scientific. The constant current supplier was similar to the one used in batch experiments. All piping connections are made of either Teflon® or stainless steel.

The feed solution containing DNT and ethanol or TNT and RDX is prepared in the two large feed tanks. The solution is pumped into the reactor using one of the positive displacement pumps at the desired flow rate. A 0.25M sodium sulfate solution is used as the salt solution. The salt solution is pumped through the Teflon® tube in the reactor in a closed loop and is changed when a considerable decrease in conductivity is observed. The rate of pumping of salt solution is maintained constant at 20L/day. The third pump is used to recycle part of the effluent into the reactor. The same procedures as described for the batch process are used to analyze the samples from the effluent stream. In addition, the conductivity of the salt solution and the dissolved oxygen content of the effluent are monitored at least three times per day.

4 Results and Discussion

Batch Reactor

Previous studies by Meenakshisundaram et al. (1999) and Pehkonen et al. (1999) showed the optimal values of various parameters for the electrochemical degradation of nitroaromatics in a batch reactor. Table 2 lists these conditions. In the current study, the propellant wastewater and pinkwater are simulated in the laboratory by adding the required amounts of nitroaromatics to water. The electrochemical reduction experiments were conducted in the batch reactor.

Propellant wastewater was simulated by preparing a solution of 100 mg/L of DNT and 300 mg/L of ethanol in deionized water. The pink water was simulated by adding 70 mg/L of TNT and 10 mg/L of RDX to deionized water. These concentrations of DNT and TNT and RDX were based on U.S. Army wastewaters. Ten experiments were conducted on propellant wastewater for varying values of current and stir rates. As for the pink water, 10 experiments were conducted under open system and 10 more experiments under deoxygenated conditions. For the deoxygenated conditions the deionized water was purged with nitrogen for 3 to 4 hrs, before adding the required amounts of TNT, RDX, salt, and buffer. The reactor was then closed with a lid, which had a port for holding the pH probe for continuous monitoring of the pH during the experiment. The dissolved oxygen was measured before and after the experiments and was found to be below 0.2 mg/L.

Table 2. Summary of experimental conditions in a batch reactor.

Parameters	Values
Reactor volume	2000 mL
Salt concentration	36 g/L
pH	8.0
Applied current	23mA - 65mA
Stir rate	630, 2040 rpm
Electrodes	Glassy Carbon
Surface area	67.5 cm^2
Porosity	0
Dissolved oxygen	0.2 mg/L (deoxygenated) 8.4 mg/L (open system)

Experiments were carried out at five different current settings: 23, 34, 45, 53, and 65 mA. The Honeywell UDC is capable of providing a constant current input to the electrodes. Two different speed settings of the stirrer for a given applied current were used: 630 and 2040 rpm. These stir rates correspond to calibration points 4 and 5 labeled on the stirrer. The pseudo first order rate constants were obtained by plotting the natural log of the nitroaromatic concentration in ppm versus time in minutes. The slope of the curve gives the reduction rate constant. Only kinetic data with an R^2 value more than 0.95 are reported.

Electrochemical Reduction of 2,4-Dinitrotoluene (DNT)

Batch experiments were conducted to study the electrochemical reduction of simulated propellant wastewater. Table 2 lists the rate constants for the reduction of DNT. The current was varied between 23 and 65 mA, and experiments were conducted for stir rates of 630 and 2040 rpm for each current. The last column in Table 3 shows the rates constants for reduction of DNT obtained by a previous study (Meenakshisundaram et al. 1999).

The rate constants varied between 0.0026 and 0.0063 min^{-1}. The rate constants for different stir rates were plotted as a function of the current. Figure 3 shows that the reduction rate constants increase with an initial increase in current, but flatten out at higher current values. The reason for the flattening of the curve is speculated to be mass transfer limitations.

Table 3. Rate constants for reduction of DNT in a batch reactor.

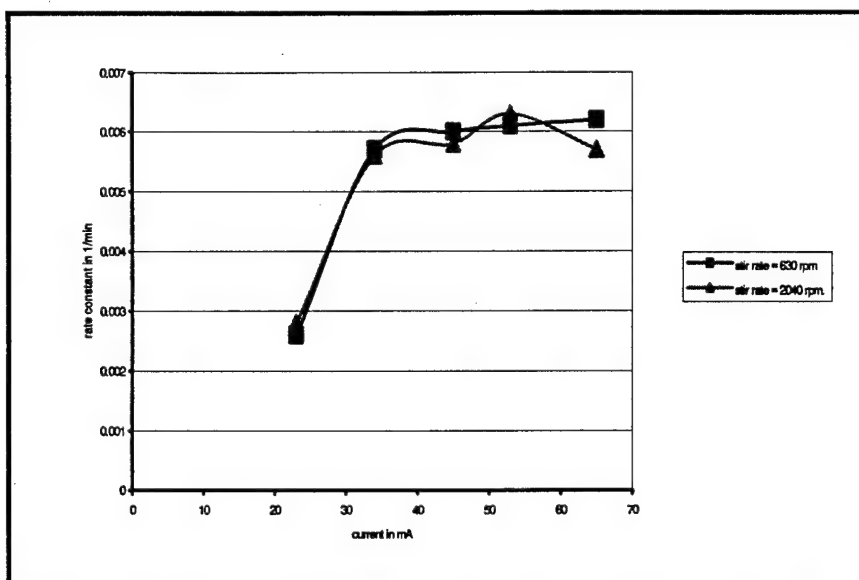| Current (mA)	Stir Rate (rpm)	Ethanol (mg/L)	pH	Rate (min^{-1}) for 100 ppm DNT	Rate (min^{-1}) for 50 ppm DNT (Meenakshisundaram et al. 1999)
23	630	300	8.0	0.0026	0.0026
34	630	300	8.0	0.0057	0.0036
45	630	300	8.0	0.006	0.0050
53	630	300	8.0	0.0061	0.0056
65	630	300	8.0	0.0062	0.0060
23	2040	300	8.0	0.0028	—
34	2040	300	8.0	0.0056	—
45	2040	300	8.0	0.0058	0.0052
53	2040	300	8.0	0.0063	0.0056
65	2040	300	8.0	0.0057	0.0061

Figure 3. Variation of rate constant for reduction of DNT with current.

Meenakshisundaram et al. (1999) has also observed this. At lower currents the rate of the reaction plays a major role in the rate constant, whereas at higher currents the mass transfer limitations govern the rate constants. The nitroaromatic at such high current is not able to reach the cathode at the same rate as the electrons are produced. Hence, the efficiency of reduction would decrease and more hydrogen gas would evolve. No considerable change in reduction rate is observed for a change in the stir rate.

End product studies conducted for three experiments were used to calculate the molar conversion of DNT to other products. Table 4 lists the results. An approximate 90 to 100 percent mass balance (on a molar basis) was achieved for experiments conducted with DNT. An important finding from this study is that most of the products are present in the solid phase, which is formed during the experiment. Only DAT is found in the aqueous phase.

Electrochemical Reduction of Pink Water in an Open Batch Reactor

Batch experiments in an open system were conducted to study the electrochemical reduction of simulated pinkwater. The current was varied between 23 and 65 mA and the experiments were conducted for two values of stir rate for each current. Table 5 lists the rate constants for the reduction of TNT and RDX. The data in Table 5 show that the rate constant for the reduction of TNT varies between 0.0017 and 0.0077 min^{-1}, and the rate constant of RDX varies between 0.0013 and 0.0066 min^{-1}.

Table 4. Mass balance of DNT in a batch reactor.

Current (mA)	Compounds	Solid Phase (% molar conversion of DNT to)	Aqueous phase (% molar conversion of DNT to)
25	4-nitro, 2-nitroso toluene	42.26	—
	2-nitro, 4-aminotoluene	38.39	—
	2,4-diaminotoluene	—	15.29
65	4-nitro, 2-nitrosotoluene	35.79	—
	2-nitro, 4-aminotoluene	33.99	—
	4-nitro,2-aminotoluene	2.62	—
	2,4-diaminotoluene	—	14.47
53	4-nitro, 2-nitrosotoluene	14.9	—
	2-nitro, 4-aminotoluene	72.68	—
	4-nitro, 2-aminotoluene	3.12	—
	2-nitro, 4-nitrosotoluene	0.14	—
	2,4-diaminotoluene	—	14.32

Table 5. Rate constants for reduction of TNT and RDX in an open system.

Current (mA)	Stir Rate (rpm)	pH	Rate (min^{-1}) for degradation of TNT	Rate (min^{-1}) for degradation of RDX
65	2040	8.0	0.0063	0.0059
53	2040	8.0	0.0077	0.0066
45	2040	8.0	0.0069	0.0055
34	2040	8.0	0.0061	0.005
25	2040	8.0	0.002	0.0014
65	630	8.0	0.006	0.0042
53	630	8.0	0.0062	0.0048
45	630	8.0	0.0055	0.0044
34	630	8.0	0.0053	0.0035
25	630	8.0	0.0017	0.0013

Figures 4 and 5 show the variation of rate constant with current for TNT and RDX, respectively, for different stir rates. Figures 4 and 5 show that the rate constant increases with the initial increase in current and flattens out at higher values of current. Mass transfer limitations are again speculated to be the reason for the relative decrease in rate constants for a steady increase in current. It can also be observed that the rate constants decrease with a decrease in the stir rate. The difference in rate constants for low stir rate for the different currents studied is less than the difference observed for high stir rate. This can be attributed to the fact that more mixing causes a smaller diffusion layer on the cathode, thus reducing the mass transfer limitations. At the low current value (23 mA), very little difference between the two stir rates is observed. It is speculated that at such low current, value mass transfer limitations play a minor role. End product studies conducted for seven experiments were used to calculate the molar conversion of TNT to other products. Table 6 lists the results.
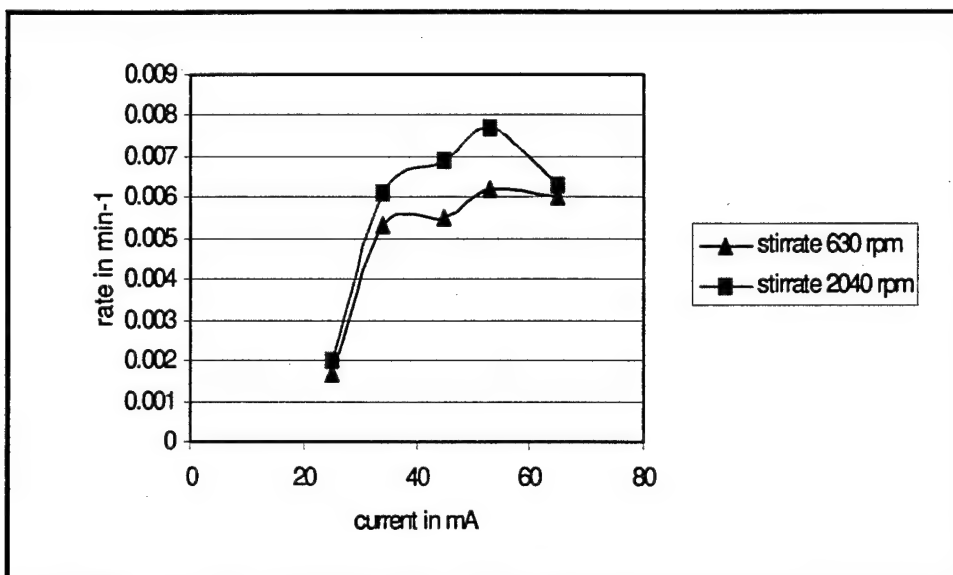
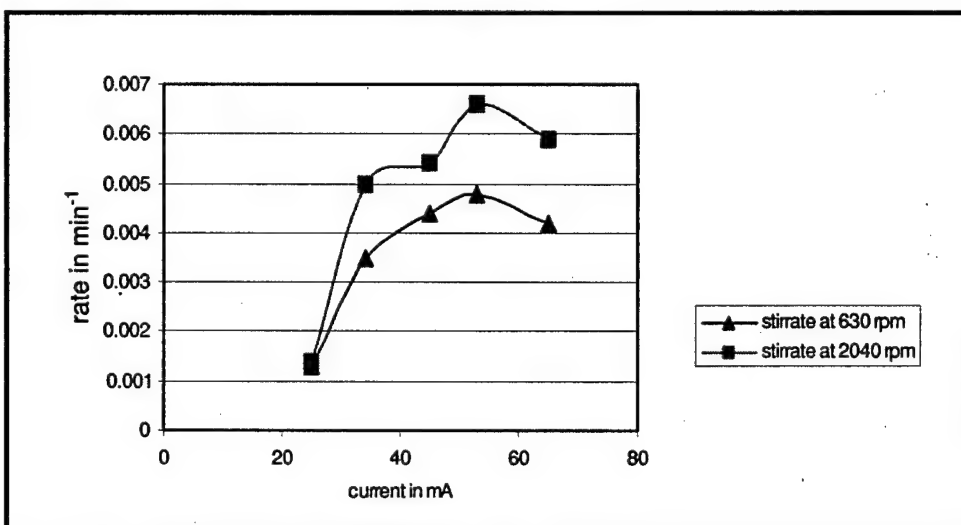**Figure 4. Variation of rate constant of TNT with current.**

Figure 5. Variation of rate constant of RDX with current.

The data in Table 6 show that approximately 60 to 100 percent mass balance could be accounted for in for all the experiments. Most of the end products are observed to be in the solid phase. In the table, Dimer 1 indicates 2,2',4,4'-tetranitro-6,6'-azoxytoluene and Dimer 3 indicates 4,2',6,6'-tetranitro-2,4'-azoxytoluene. The other dimer, 4,4',6,6'-tertranitro-2,2'-azoxytoluene could not be calibrated on the HPLC and hence could not be identified.

RDX was expected to yield mono-, di-, and tri-nitroso substitutes of nitro groups in RDX commonly called MNX, DNX and TNX respectively. Since these compounds are not commercially available and no published methods of synthesis could be obtained, the intermediates of RDX could not be confirmed or quantified.

Table 6. Mass balance for TNT in an open batch reactor.

Current (mA)	Stir Rate (rpm)	Compounds	% molar conversion of TNT to the compound (solid phase)	% molar conversion of TNT to the compound (Aqueous phase)
45	2040	2-Amino-4,6-dinitrotoluene	2.5	—
		Dimer 1	35.35	—
		Dimer 3	19.05	—
		TNT	—	5.19
25	2040	2-Amino-4,6-dinitrotoluene	2.02	—
		4-Amino-2,6-dinitrotoluene	—	2.89
		2,4-Diamino-4-nitrotoluene	—	2.72
		Dimer 1	61.20	—
		TNT	—	18.83
65	630	2-Amino-4,6-dinitrotoluene	1.83	1.88
		2,6-Diamino-4-nitrotoluene	—	3.26
		Dimer 1	14.55	—
		Dimer 3	21.38	—
		TNT	—	12.11
53	630	2-Amino-4,6-dinitrotoluene	3.55	—
		Dimer 1	16.95	—
		Dimer 3	22.67	—
		TNT	—	10.49
45	630	Dimer 1	30.05	—
		Dimer 3	29.3	—
		TNT	—	6.7
34	630	2-Amino-4,6-dinitrotoluene	3.67	—
		Dimer 1	77.67	—
		Dimer 3	16.95	—
		TNT	—	4.15
25	630	2-Amino-4,6-dinitrotoluene	7.40	—
		4-Amino-2,6-dinitrotoluene	—	2.29
		Dimer 1	20.91	—
		Dimer 3	37.42	—
		TNT	—	26.20

Reduction of Pink Water under Deoxygenated Conditions

Electrochemical batch experiments were also conducted to study the reduction of TNT and RDX (pink water) in anoxic (or deoxygenated) conditions. Ten experiments were conducted for various values of current (23, 34, 45, 53, and 65 mA) and two different stir rates (630 and 2040 rpm). Table 7 lists the rate constants for the reduction of TNT and RDX.

Table 7. Rate constants for reduction of TNT and RDX under deoxygenated conditions.

Current (mA)	Stir Rate (rpm)	pH	Rate (min^{-1}) for degradation of TNT	Rate (min^{-1}) for degradation of RDX
65	2040	8.0	0.0009	0.0007
53	2040	8.0	0.0020	0.0002
45	2040	8.0	0.0009	0.0003
34	2040	8.0	0.0006	0.0002
25	2040	8.0	0.0006	0.0002
65	630	8.0	0.0005	0.0005
53	630	8.0	0.0009	0.0006
45	630	8.0	0.0007	0.0001
34	630	8.0	0.0008	0.0001
25	630	8.0	0.0003	0.0001

The data in Table 7 show that the rate of TNT varies between 0.0003 and 0.002 min^{-1}, whereas the rate of reduction of RDX varies between 0.0001 and 0.0007 min^{-1}. A comparison of these rate constants with the rate constants in Table 5 shows that there is a significant decrease in rate of reduction of pink water between open system and deoxygenated conditions.

Further experiments need to be conducted under anoxic conditions in the presence of iron salt to determine if the presence of iron (presumably, acting as a catalyst) will allow a significant reduction of TNT and RDX. Also, to fully understand the role of the presence of dissolved oxygen in the reduction process, experiments need to be conducted under different levels of dissolved oxygen concentration. Figures 6 and 7 show the rate constants of TNT and RDX for different stir rates as a function of current. These figures demonstrate that the rate constant shows very small variation with current.
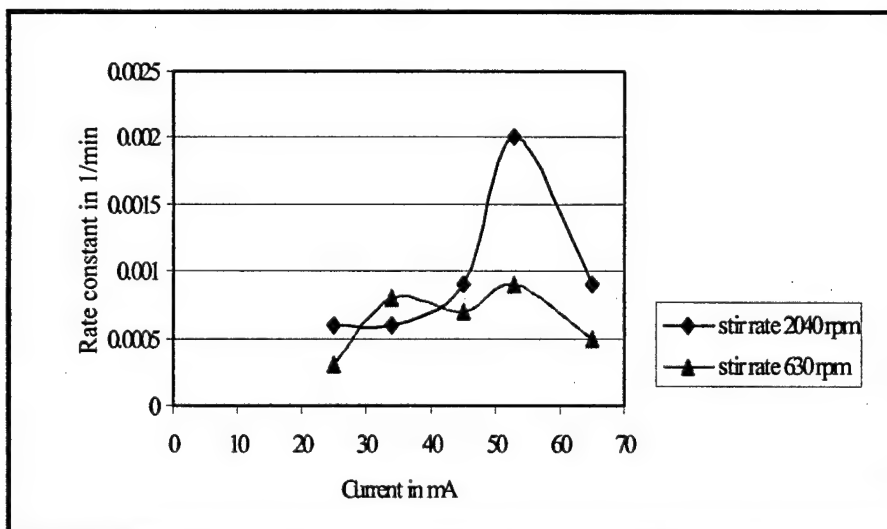

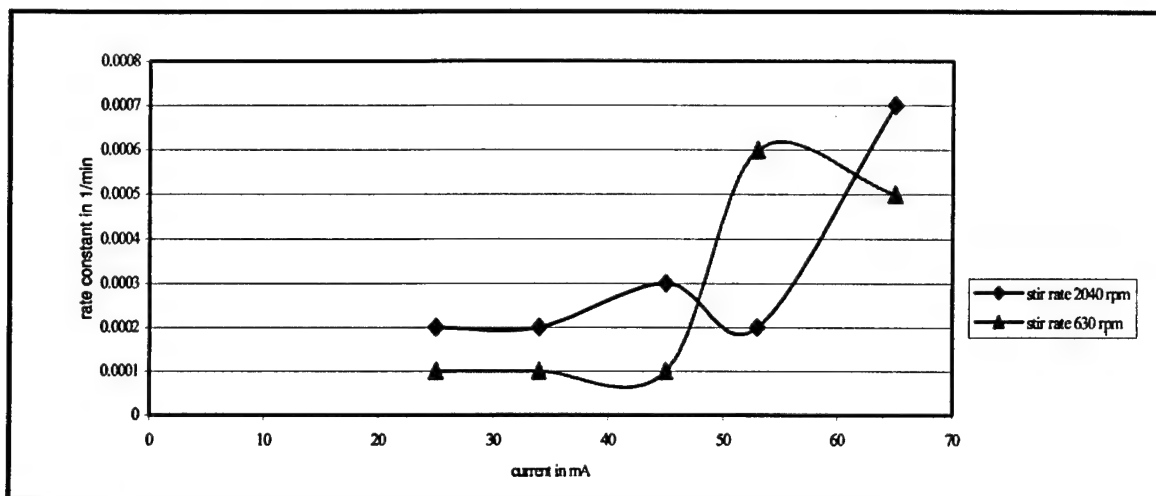Figure 6. Variation of rate constant of TNT with current for anoxic conditions.

Figure 7. Variation of rate constant of RDX with current for anoxic conditions.

Table 8. Rate constants for reduction of TNT and RDX under deoxygenated conditions.

Current (mA)	Stir Rate (rpm)	pH	Rate (min⁻¹) for degradation of TNT	Rate (min⁻¹) for degradation of RDX
65	2040	8.0	0.0009	0.0007
53	2040	8.0	0.0020	0.0002
45	2040	8.0	0.0009	0.0003
34	2040	8.0	0.0006	0.0002
25	2040	8.0	0.0006	0.0002
65	630	8.0	0.0005	0.0005
53	630	8.0	0.0009	0.0006
45	630	8.0	0.0007	0.0001
34	630	8.0	0.0008	0.0001
25	630	8.0	0.0003	0.0001

Table 8 shows the mass balance of TNT in the anoxic conditions. Since the data show a very low degradation, the mass balance studies could be conducted only for four experiments. As the data in Table 8 show, about 70 to 80 percent of the mass balance could be attained. Most of the TNT still remains in the solution, which explains the low rate of reduction. Also, equal amounts of end products were observed in the solid and the aqueous phases.

Pilot Scale Flow Through Reactor

Experiments were conducted in the pilot scale flow-through reactor using the simulated munitions wastewater. At the time of this report, only the experiments with DNT and ethanol had been conducted. Table 9 lists the changes made to the operational parameters over time. The effluent solution was analyzed for DAT starting at day 40.

Table 9. Parameters changed with time for continuous flow reactor.

Time in Days	Parameters
Day 1 (4/3/2000)	Current = 25 mA, Flow rate = 6 L/day Recycle = 3 L/day, pH = 8, DNT = 100mg/L, Ethanol = 300 mg/L, Buffer = 0.02 mg/L, Anode solution = 0.25 M Na_2SO_4
Day 9	Current changed to 34 mA
Day 14	Experiment stopped to clean salt solution tank due to bacterial slime growth on walls of the salt solution tank.
Day 15	Experiment restarted
Day 24	Recycle increased to 4.5 L/day
Day 31	Current changed to 45 mA
Day 43	Recycle increased to 6 L/day
Day 45	Current changed to 53 mA Salt added to feed solution =100 mg/L NaCl
Day 51	Current changed to 65 mA
Day 53	Salt added to feed solution =300 mg/L NaCl
Day 61	Salt added to feed solution = 1 g/L NaCl
Day 63	New anode solution was prepared
Day 67	Salt added to feed solution = 5 g/L NaCl
Day 74	Salt added to feed solution = 10 g/L NaCl
Day 78	Feed flow rate increased to 13.75 L/day

The current in the reactor was maintained at 25 mA from day 1 to day 9. The maximum DNT reduction observed during this period was about 28 percent and the minimum was about 8 percent. The average reduction during this period was 15 percent. The voltage observed at this current was 2.1 V.

On day 9, the current was increased to 34 mA and maintained at this level up to day 31. During this period, the recycle was also increased to 4.5 L/day. The maximum reduction during this period was about 30 percent, whereas the minimum was about 8 percent. The voltage during this period was 2.2 V. The average reduction during this period was about 17 percent. On day 31, the current was increased to 45 mA and maintained at this level up to day 45. The minimum and maximum reductions observed were about 8 and 18 percent, respectively. The average reduction during this period was about 15 percent. The voltage measured during this period was 2.3 V.

For the next 5 days (day 45 to day 51), the current was maintained at 53 mA. The maximum and minimum reductions were 15 and 9 percent, respectively. The average reduction observed was about 13 percent. The voltage at this current was 2.4 V.

The above summary indicates that the percent reduction of DNT was, on average, about 15 percent, without respect for the current values. It is thus speculated that there are mass transfer limitations in the cathode compartment of the reactor. To overcome these limitations, a salt solution needs to be added to increase the conductivity of the cathode compartment. It was decided to add NaCl in the feed solution so that the concentration of the salt is only 100 mg/L. The salt solution has increased the conductivity of the feed solution to only 3.68ms/cm compared to 3.48 ms/cm prior to the addition of the salt. The increase in conductivity was only 0.2 ms/cm; no significant difference in reduction of DNT was observed. Further experiments were conducted by steadily increasing the salt solution to determine the optimum conductivity that will significantly reduce the DNT to appreciable low levels in the effluent stream (see Table 9). Figure 8 shows the variation of concentration of DNT and efficiency of removal of DNT with time.

The vertical lines in the figure indicate the various current changes. There was no appreciable increase in degradation of DNT with increase in salt content to the feed solution. Hence, the mass transfer limitations may be attributed to the fact that the flow rate is low enough to affect significant diffusion in the wide cathode compartment. Also, inspection of the anode compartment has shown that the Nafion membrane was deformed. (It was corrugated along the length of the reactor.) To avoid such a deformation, the Nafion membrane should be woven with cloth to retain rigidity.
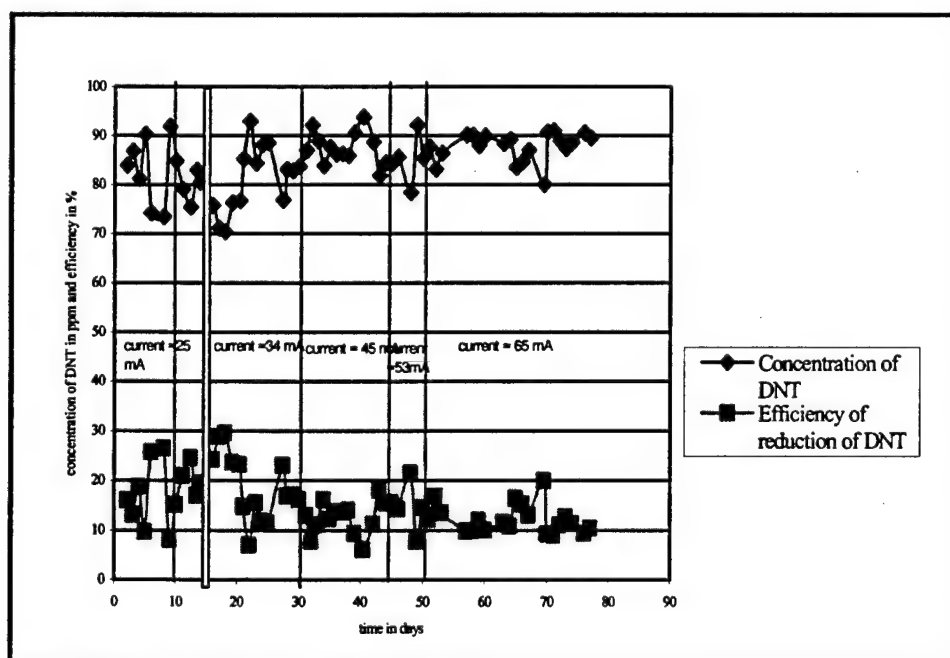

Figure 8. Concentration of DNT and efficiency of removal as a function of time.

Figures 9, 10, and 11 show the variations of flow rates, and pH and salt solution conductivity, respectively, as a function of time. Figure 9 shows that the average flow rate was about 6.0, but there were significant fluctuations in the flow rate with the change of the pressure in the feed tank. To maintain a constant pressure, a manometer will be attached to the feed tank. This will allow the change in the pressure to be observed so that the necessary adjustments can be made to (increase) the pressure of nitrogen in the tank.

Figure 10 shows that initial measurements of pH returned low values of about 7.35. After 15 days from the start of the reactor, the pH was observed to be constantly increasing and some amounts of H_2SO_4 were added to maintain the pH at about 8.0. Figure 11 shows that the salt solution conductivity decreases steadily with time. A new salt solution was prepared on day 62, when the conductivity fell to 20 ms/cm.
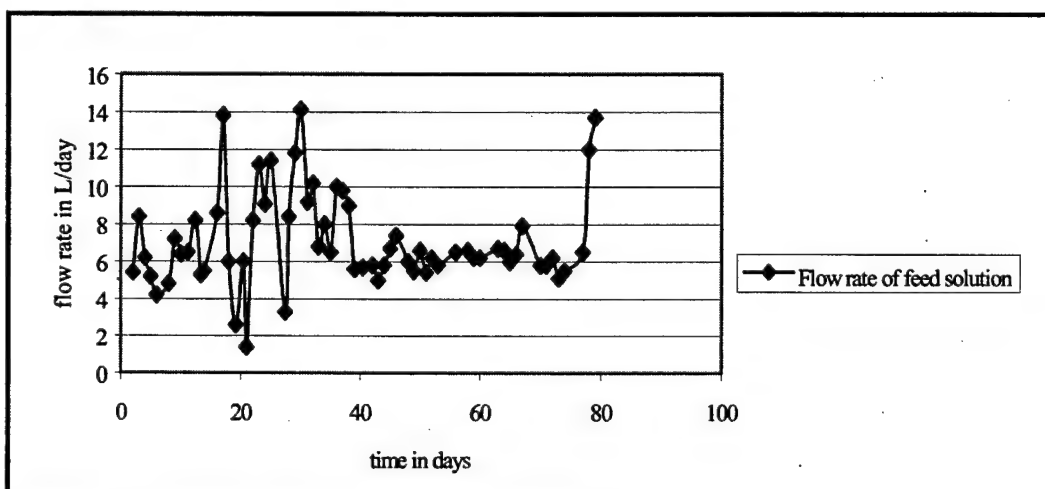

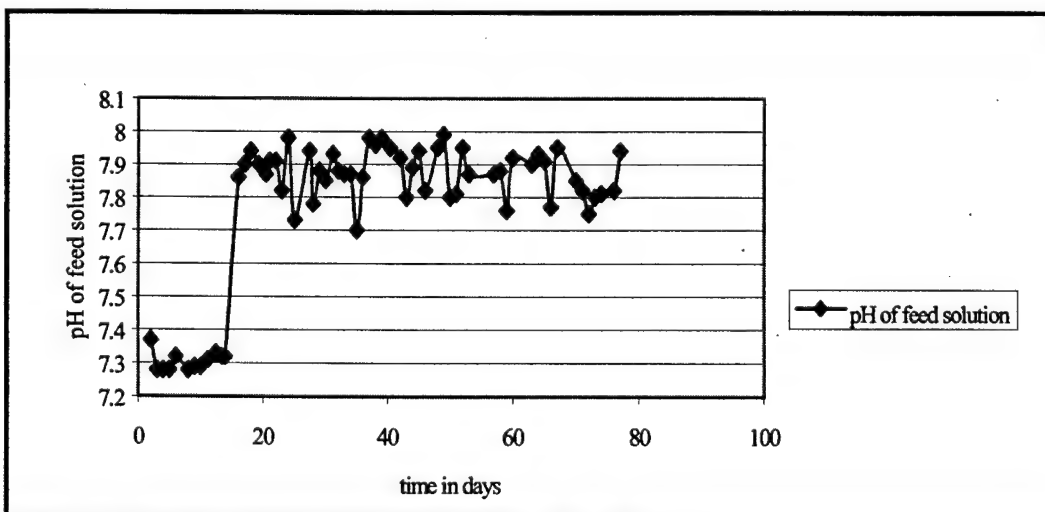Figure 9. Flow rate vs. time for flow through reactor.
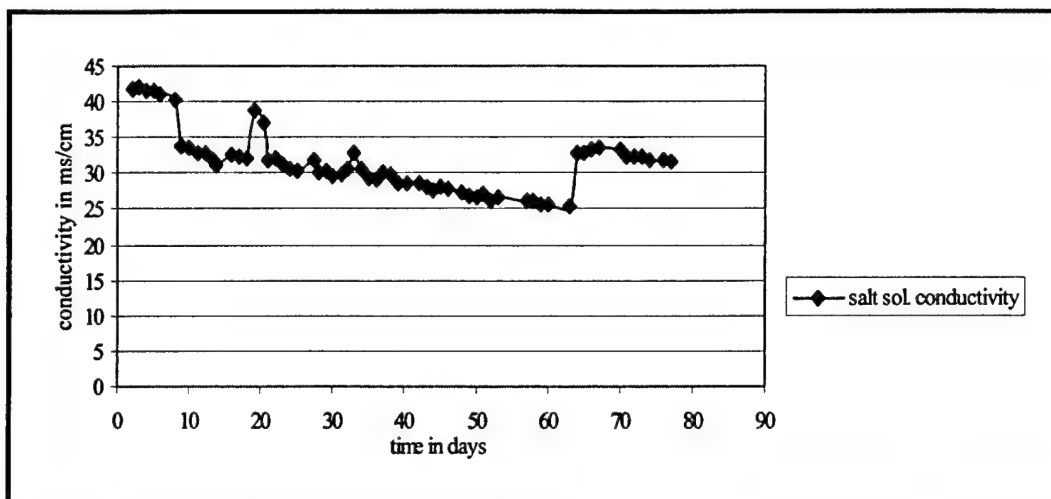

Figure 10. pH of solution as a function of time.

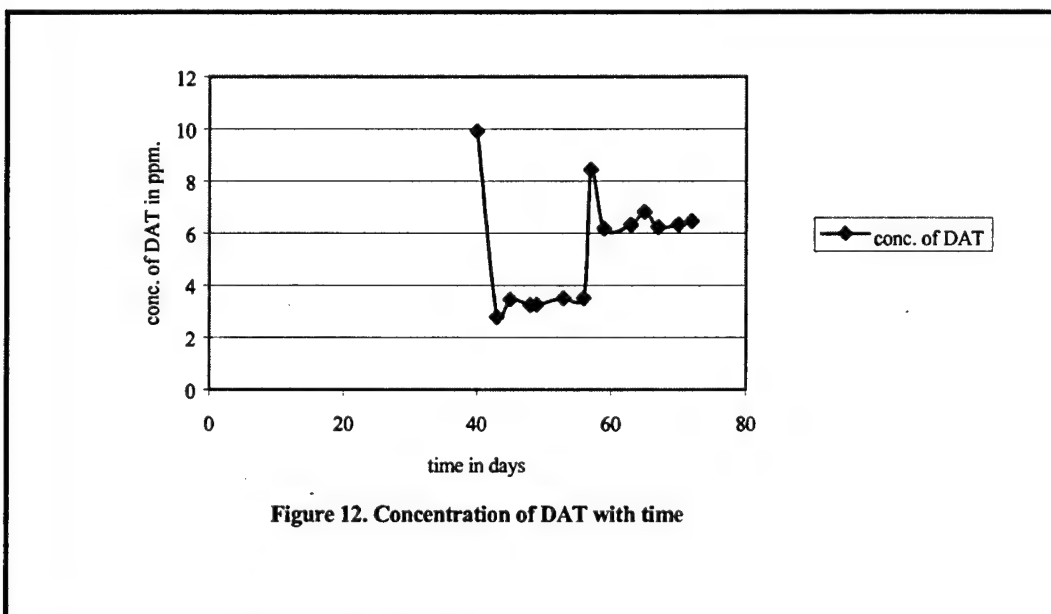**Figure 11. Variation of salt conductivity with time.**

Figure 12. Concentration of DAT with time

Figure 12. Concentration of DAT with time.

DAT concentrations in the effluent stream were determined starting from day 40. Figure 12 shows the concentration of DAT in the effluent stream with time. This figure shows that the molar conversion to DAT accounts to about 90 percent of the DNT disappearance.

5 Conclusions and Recommendations

Conclusions

The results of the batch reactor tests in the presence and absence of dissolved oxygen have shown that both propellant and pinkwater can be effectively electrochemically reduced.

The products resulting from electrochemical reduction of TNT were two kinds of azoxy dimers and various amino-substitutes of the nitro groups. The products resulting from electrochemical reduction of DNT were primarily DAT and the amino analogs of nitro groups. A large fraction of the intermediates was observed in the solid phase.

The reduction rates for DNT, TNT, and RDX were observed to increase with an increase in current, but at higher currents, the mass-transfer rates govern the reduction rates. The rates of reduction were also observed to increase with an increase in stir rates.

Recommendations

The reduction of TNT and RDX under anoxic conditions was significantly lower compared to the results obtained in the presence of dissolved oxygen. To fully explain the role of dissolved oxygen in the electrochemical reduction, it is recommended that a further set of experiments be conducted under a different level of dissolved oxygen (30 mg/L). This condition is achieved by purging the reactor water with oxygen prior to the addition of the compounds of concern, and then by maintaining the reactor under oxygen. Also, further experiments need to be conducted under anoxic conditions in the presence of iron salt to determine if the presence of iron (presumably, acting as a catalyst) will allow a significant reduction of TNT and RDX.

The results obtained to date from the pilot scale reactor showed very low reduction efficiency for DNT. To be able to determine if the low reduction is due to mass transfer limitations, adding salt in the feed solution increased the conductivity of the cathode compartment. However, no improvement in the reduction of

DNT was observed. It is speculated that the low flow rate and the wide cathode compartment may have played a major role in the mass transfer limitations. Also inspection of the Nafion membrane has shown that it was corrugated along the whole length of the reactor. To avoid such deformation, it is recommended that the Nafion membrane be woven with cloth to retain rigidity. It is also recommended to narrow the annular space between the anode and the cathode by increasing the diameter of the anode compartment and using a rigid Nafion membrane to improve mass transfer within the cathode compartment.

References

Berchtold, S.R., S.L. VanderLoop, M.T. Suidan, and S.W. Maloney, "Treatment of 2,4-Dinitrotoluene Using a Two-Stage System: Fluidized-Bed Anaerobic Granular Activated Carbon Reactors and Aerobic Activated Sludge Reactors," *Water Environ. Res*, No. 67 (1995), pp 1081-1091.

Boopathy R., M. Wilson, and C.F. Kulpa, "Anaerobic Removal of TNT Under Different Electron Acceptor Conditions: Lab Study," *Water Environ. Res.*, No. 55 (1993), pp 271-275.

Cheng, J., M.T. Suidan, and A.D. Venosa, "Abiotic Reduction of 2,4-Dinitrotoluene in the Presence of Sulfide Minerals Under Anoxic Conditions," *Water Sci. Tech.*, vol 34, No. 10 (1996), pp 25-33.

Fisher, R.H., and J.M. Taylor, *Munitions and Explosive Wastes* (Noyes Data Corporation, Park Ridge, NJ, 1983), pp 297-303.

Fry, A.J., "Electrochemistry of Nitro Compounds," in *The Chemistry of Amino, Nitroso, and Nitro Compounds and Their Derivatives*, vol 1, S. Patai, ed. (Wiley-Interscience: Chichester, 1982), pp 319-337.

Haidour, A., and J.L Ramos, "Identification of Products Resulting from the Biological Reduction of TNT and DNT by *Pseudomonas sp*," *Environ. Sci. Technol.*, No. 30 (1996), pp 2365-2370.

Hao, O.J., K.K. Phull, A.P. Davis, J.M. Chen, and S.W. Maloney, "Wet Air Oxidation of Trinitrotoluene Manufacturing Red Water," *Water Environment Res.*, No. 65 (1993), pp 213-220.

Ho, P.C., and C.S. Daw., "Adsorption and Desorption of Dinitrotoluene and Activated Carbon," *Environ. Sci. Tech*, No. 22 (1988), pp 991-24.

Janssen, H.J., A.J. Kruithof, G.J. Steghniuis, and Westerterp, "Kinetics of the Catalyitc Hydrogenation of 2,4-Dinitrotoluene," *Ind. Eng. Chem. Res.*, No. 29 (1996), pp 754-66.

Jenkins, T., and M. Walsh, *Field Screening Methods for Munitions Residues in Soils, Semiarid Technologies for Remediating Sites Contaminated with Explosive and Radioactive Waste*, EPA/625/K93/001 (Office of Research and Development, Washington, DC, 1993).

Jolas, J.L., S.O. Pehkonen, and S.W. Maloney, "Reduction of 2,4-Dinitrotoluene with Graphite and Titanium Mesh Cathodes," *Water Environment Research*, vol 72, No. 2 (2000), pp 179-188.

Kopilov, J., and D.H. Evens, "Electrochemical Reduction of Some a-Haloacetanilides," *J. Electoanal. Chem.*, vol 208 (1990), pp 438-438.

Martiny, P., and J. Simonet, "On the Existence of the Intermediate Nitroso During the Mixed Electrochemical Reduction of Nitro Compounds and Organic Halides," *J. Electroanal. Chem.*, vol 148 (1983), pp 51-60.

Meenakshisundaram, D., M. Mehta, S. Pehkonen, and S.W. Maloney, *Electrochemical Reduction of Nitro-Aromatic Compounds*, Technical Report (TR) 99/85/ADA371059 (U.S. Army Construction Engineering Research Laboratory [CERL], October 1999).

Parrish, F.W., "Fungal Transformation of 2,4-Dinitrotoluene and 2,4,6-Trinitrotoluene," *App. Environ. Micro. Biol.*, vol 47 (1997), pp 1295-98.

Pehkonen, S.O., J.L. Jolas, D. Meenakisundaram, and S.W. Maloney, *Electrochemical Reduction of Dinitrotoluene*, TR 99/89/ADA372795 (CERL, November 1999).

Ribordy, P., C. Pulgarin, J. Kiwi, and P. Peringer, "Electrochemical versus Photochemical Pretreatment of Industrial Wastewaters," *Water Sci. Tech*, vol 35, No. 4 (1997), pp 293-302.

Sax, N.I., and R.J. Lewis, *Dangerous Properties of Industrial Materials*, 7th ed. vol 2,3 (Von Nostrand Reinhold, New York, 1989).

Schmelling D.C., and K.A. Gray, "Photocatalytic Transformation and Mineralization of TNT in TiO_2 Slurries," *Water Research*, vol 29 (1995), pp 2651-2662.

Schmelling, D.C., K.A. Gray, and P.V. Kamat, "Role of Reduction in the Photocatalytic Degradation of TNT," *Environ. Sci .Tech*, vol 30 (1996), pp 2547-2555.

Simonsson, D., "Electrochemistry for a Cleaner Environment," *Chemical Society Reviews*, vol 26 (1997), pp 181-189.

Tri-Service Reliance Joint Engineers-Environmental Quality Technical Area Panel, *Triservice Environmental Quality Strategic Plan Program*, Draft Program User Review (Fort Belvoir, VA, 1992).

Willberg, D.M., P.S. Lang, R.H. Hochemer, A. Kratel, and M.R. Hoffmann, "Degradation of 4-chlorophenol, 3,4-dichloroaniline and 2,4,6-trinitrotoluene in an Electrohydraulic Discharge Reactor," *Environ. Sci. Technol.*, vol 30 (1996), pp 2526-2534.

Young, D.M., C.L. Kitts, P.J. Unkefer, and K.L. Ogden, "Biological Breakdown of RDX in Slurry Reactors," *Biotechnol. Bioeng.*, vol 56 (1997), pp 258-267.

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14. ABSTRACT

TNT, DNT, and RDX are major constituents of munitions production wastewaters. DNT enters waste-streams during propellant production, whereas TNT and RDX enter waste-streams during munitions loading and demilitarization. This study evaluated the rate kinetics of electrochemical reduction of simulated wastewater containing similar organic strength as found in the Army munitions wastewaters. Experiments to study the electrochemical reduction of DNT in the presence of ethanol and a mixture of TNT and RDX were conducted for various electrical currents and two different stir rates, and also in the presence and absence of oxygen. The study also tested the performance of a continuous flow-through pilot scale reactor for electrochemical reduction of simulated munitions wastewaters. High pressure liquid chromatography was used for analysis in TNT and RDX experiments. The intermediate products of RDX could not be quantified and hence only qualitative analysis of RDX intermediate products were presented. The results of the batch reactor tests in the presence and absence of dissolved oxygen or solution showed that both propellant and pinkwater can be effectively electrochemically reduced.

15. SUBJECT TERMS
hazardous waste minimization, industrial wastewater treatment, electrochemical degradation, munitions waste disposal, pinkwater, 2,4,6 - trinitrotoluene (TNT)

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